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Release and uptake of volatile inorganic and organic gases through the snowpack at Niwot Ridge, Colorado

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Abstract Whole air drawn from four heights within the high elevation (3,340 m asl), deep, winter snowpack at Niwot Ridge, Colorado, were sampled into stainless steel canisters, and subsequently analyzed by gas chromatography for 51 volatile inorganic and organic gases. Two adjacent plots with similar snow cover were sampled, one over bare soil and a second one from within a snow-filled chamber where Tedlar/Teflon-film covered the ground and isolated it from the soil. This comparison allowed for studying effects from processes in the snowpack itself versus soil influences on the gas concentrations and fluxes within and through the snowpack. Samples were also collected from ambient air above the snow surface for comparison with the snowpack air. Analyzed gas species were found to exhibit three different kinds of behavior: (1) One group of gases, i.e., carbon dioxide (CO_2), chloroform ($CHCl_3$), dimethylsulfide $(CH_3)_2S$, carbondisulfide (CS_2), and dichlorobromomethane ($CHBrCl_2$), displayed higher concentrations inside the snow, indicating a formation of these species and release into the atmosphere. (2) A second group of compounds, including carbon monoxide (CO), carbonyl sulfide (COS), the hydrocarbons methane, ethane, ethyne, benzene, and the halogenated compounds methylchloride (CH_3Cl), methylbromide (CH_3Br), dibromomethane (CH_2Br_2), bromoform ($CHBr_3$), tetrachloromethane (CCl_4), CFC-11, CFC-12, HCFC-22, CFC-113, 1,2-dichloroethane, methylchloroform, HCFC-141b, and HCFC-142b, were found at lower concentrations in the snow, indicating that the snow and/or soil constitute a sink for these gases. (3) For 21 other gases absolute concentrations, respectively concentration gradients, were too low to unequivocally identify their uptake or release behavior. For gases listed in the first two groups, concentration gradients were incorporated into a snowpack gas diffusion model to derive preliminary estimates of fluxes at the snow-atmosphere interface. The snowpack gradient flux

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technique was found to offer a highly sensitive method for the study of these surface gas exchanges. Microbial activities below this deep, winter snowpack appear to be the driving mechanism behind these gas sources and sinks. Flux results were applied to a simple box model to assess the potential contribution of the snowpack uptake rates to atmospheric lifetimes of these species.

Keywords Snow · Soil · Winter · Fluxes · Volatile inorganic and organic gases · CFC · HCFC · Hydrocarbons

Introduction

Gas exchanges between snow and the atmosphere have been receiving increasing research attention. This interest is driven by new evidence that supports the important influence of snow chemistry and physics on surface exchanges, atmospheric processes, and soil biogeochemistry underneath the snowpack. Identified reservoirs for chemical reactions resulting in gas formation with subsequent exchanges at the snowpack surface can be differentiated in these main processes:

1. Snow carries trace amounts of inorganic and organic impurities that stem from natural and anthropogenic sources. It has long been known that precipitating snow constitutes an input of these contaminants into the environment. A plethora of research has been dedicated to this topic, with particular emphasis on inputs of semi-volatile organic compounds and mercury because of their toxic properties in ecosystems (Franz and Eisenreich 1998; Ariya et al. 2004).
2. Contaminants can be deposited from the gas phase to snow on the ground by dry deposition. This process causes increased levels of trace constituents in the snow as the snowpack ages and has been found responsible for increased levels of many persistent organic pollutants in the arctic environment (Blais et al. 1998).
3. Newer research conducted over the past 10 years has provided increasing evidence that solar irradiance triggers a rather active photochemistry involving trace constituents in the uppermost layers of the snowpack, and that these reactions constitute sources and sinks for gases in the atmosphere (Domine and Shepson 2002). Most of this research has been conducted in Polar Regions, with a particular emphasis on the radical and oxidation chemistry in and above the snowpack (Dibb et al. 2007; Grannas et al. 2007; Eisele et al. 2008).
4. Snow on the ground, in particular, deep and long-lasting winter snowpack has also been found to play an important role in modulating biogeochemical processes in the subniveal (underneath the snow) soil. Such conditions are mostly encountered in higher elevation and high latitude environments. Here, the all-winter snow cover provides insulation that allows subniveal soil to warm up to, and maintain near-freezing temperature at constant moisture conditions. This system resembles a low-temperature incubator. Despite the ~zero-degree temperature regimes, this environment has been found to support an active microbial community promoting wintertime respiration processes, which result in elevated interstitial gas concentrations and exchanges through the snowpack (Monson et al. 2006; Nobrega and Grogan 2007).

In this research, we further address emerging questions related to the latter process (4). Previous studies have mostly investigated how the snowpack affects exchanges of CO_2, with results unanimously pointing towards a considerable wintertime CO_2 release from the soil through the snowpack into the atmosphere [Liptzin et al. (2009) and references therein]. Only recently, this research has been extended to other climate-forcing gases, including nitrous oxide (N_2O) (Filippa et al. 2009), nitrogen oxides (NO, NO_2) (Helmig et al. 2009), and a suite of volatile inorganic and organic compounds (Swanson et al. 2005). Similar to findings about CO_2, this research has yielded evidence for the wintertime production and efflux of these gases into the atmosphere. New quantifications and characterization of these processes are presented in the aforementioned and other contributions to this special issue (Bowling et al. 2009; Seok et al. 2009). Here, we focus on a suite of trace gases including hydrocarbons, oxygenated volatile organic compounds, halogenated species, and nitrated volatile organic compounds. Gas concentrations were determined in air samples

withdrawn from inside the snowpack. Comparison measurements over a site with artificially suppressed soil gas flux exchanges were used to further investigate enhancement and depletion of these gases in the snowpack. Vertical concentration gradients provided insight into sources and sinks of these gases at the soil-snow and snow-atmosphere interfaces. Vertical concentration gradient data were incorporated into a diffusion transfer model for deriving estimates of surface exchange fluxes of 24 gases.

Experimental

This experiment was conducted over a 3-day intensive period, March 15-17, 2005, at the high-elevation Soddie site, at the Niwot Ridge, Colorado, Long-Term Ecological Research area (40°03′N, 105°35′W, 3,340 m asl) (NWT). Two sampling manifolds allowed for collection of air from inside the snowpack. One tower was installed over natural soil, and another one over a Tedlar sheet (Fig. 1). Both towers were equipped with a series of paired inlets, located at 0, 30, 60, 90, and 245 cm above the ground for the natural snowpack tower, and at 0, 30, and 60 cm above ground for the tower over the Tedlar sheet. More details about this experimental setup, including a plumbing diagram, are presented in Bocquet et al. (2007) and Seok et al. (2009). The sampling tower over the natural soil area was installed in fall 2004, and snow was allowed to naturally precipitate around it. All experiments using this tower were conducted without disturbing the natural snow conditions. The Teflon PFA tubing used for the sampling manifold was conditioned with high ozone-containing air (250 ppbv) prior to the field installation. The tubing and the manifold had been used and purged with snowpack and ambient air for a full winter prior to this experiment. The sampling manifold was found to transmit CO_2, ozone, and nitrogen oxide (NO) without any notable losses. The inlet at 245 cm remained above the snow throughout the winter and served as reference inlet for ambient air measurements. The second snow tower was installed $\sim$12 m south of the primary sampling tower over a light-transparent Tedlar sheet (5 μm thickness, Richmond Aircraft Products, Norwalk, CA). The snow ($\sim$1 m) over this area was removed for the installation of this tower during the first week of January 2005. The excavated 4 × 4 m area was covered with Tedlar film, and the 90-cm tall snow sampling tower, identical in design to the main tower, was placed in the center of this area without penetrating the Tedlar film (Fig. 1). Side walls, made of 1 m wide Teflon film were also installed around the edges of this square area to further minimize advective gas transport from the adjacent snowpack. The Teflon film used for these vertical side walls proved to be not nearly as strong as the Tedlar ground cover under these sub-freezing conditions, and broke in several places during installation and as the pit refilled with precipitating and blowing snow during the following weeks. We estimate that, nonetheless, the Teflon film was still providing an intact gas advection barrier for $\sim$30–80% of the vertical area along the edges of the Tedlar ground sheet. The site was visited and inspected at least once every week. The Tedlar/Teflon chamber backfilled with blowing and precipitating snow over the 2 weeks following installation. In order to further improve the isolation of the reference plot from the adjacent area, during the first day of the March 2005 intensive a $\sim$0.5 m wide trench was excavated from the snowpack surface all to the ground along the borders of the 4 × 4 m Tedlar-covered plot without disturbing the snowpack over the Tedlar cover itself.

Four sets of gradient profiles with one whole air sample at each height were collected into stainless steel canisters over the natural soil on both days. Three and five sets of samples were collected over the Tedlar-lined plot on March 15 and 17, respectively. The whole air sampling sequence was such that air was first drawn from the 245 cm ambient air inlet for 10 min, then sequentially from the four inlet heights on the natural snow tower, then finally from the three inlet heights from the tower on the Tedlar-covered area. A total of 65 samples were collected. Samples were transferred into pre-conditioned, evacuated canisters with air pulled from the manifold using a metal bellows pump (model MB-602, Senior Aerospace, Sharon, MA). The pump flow rate was restricted to 1.0 l min^{-1} in order to minimize the advection flow through the snowpack caused by the sampling procedure. After 2–5 min of purge flow at each sample depth to equilibrate the sample lines, canisters were opened and filled to 2,000 mbar pressure.

Samples were analyzed for a wide range of volatile gases by gas chromatography techniques. Canisters

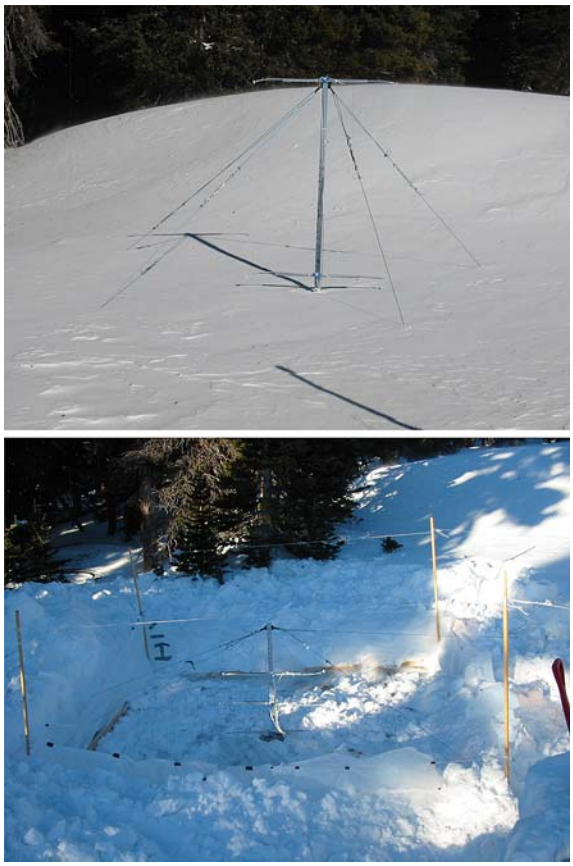

Fig. 1 *Top*: Primary snowpack sampling tower during the first week of January 2005, with lower three inlet heights (0 cm, 30 cm, 60 cm) covered by snow, and 90 cm inlet still slightly above the snow surface. The top inlet pair (at 245 cm height) remained above the snow throughout the winter season and were sampled for the ambient air reference measurement. *Bottom*: Second snow sampling tower with paired inlets at 0, 30, 60 cm over Tedlar ground cover at its installation in January 2005

were first returned to the University of California, Irvine (UCI), for analysis of methane, CO, CO_2, non-methane hydrocarbons (NMHC), oxygenated volatile organic compounds (OVOC), halocarbons, and alkyl nitrates. Subsequently, canisters were shipped to the National Center for Atmospheric Research (NCAR) for further analyses of NMHC and OVOC. The UCI analytical procedure was as follows: methane was analyzed by gas chromatography (GC) with flame ionization detection (FID). CO and CO_2 were determined by GC/FID after catalytic reduction to methane. The GC analytical system used for quantitative assay of all other gases preconcentrated the sample on a stainless steel loop filled with glass beads and immersed in liquid nitrogen, with subsequent vaporization of the entire sample. The sample concentrate was then flushed to a splitter that partitioned the flow into six different aliquots, with each separate stream directed to one of six column/detector combinations, i.e., DB-1/FID, DB-5/electron capture detection (ECD), RESTEK-1701/ECD, PLOT/FID, Cyclodex/FID, and DB-5/mass spectrometry detection (MSD). The measurement for each individual compound was taken from the most favorable column/detector combination; the data for those compounds cleanly identifiable on more than one combination were fully consistent with one another. The time between sample collection and analysis was less than 1 month for all compounds. More details for these analytical instruments and techniques are available elsewhere (Colman et al. 2001).

Multiple standards were employed. Working standards were run every two hours and calibrated standards were run twice daily. For the compounds included in this data set, analytical precision and accuracy are usually equal or better than 3%. The UCI group participated in all phases of the international non-methane hydrocarbon intercomparison experiment (NOMHICE) and achieved excellent agreement for all compounds included in this measurement evaluation (Apel et al. 2003).

For the NCAR analyses, two separate but nearly identical preconcentration systems were used, one for compound quantification by FID, and the other for MSD identification. In each case, gases were preconcentrated on a SilcoSteel® loop filled with glass beads and immersed in liquid nitrogen, and subsequently vaporized onto the head of a GC column. For the FID analysis, separation was achieved with either an HP-624 (OVOC) or DB-1 column (NMHC). For the MSD analysis, a DB-1 column (NMHC and OVOC) was used for separation. Analyses were performed within 2 months of sample collection. Multiple standards were employed including a NIST SRM propane and a NIST-certified butane and benzene standard. Further analytical details can be found in Apel et al. (2003). Data for light alkenes, OVOC, and some identified terpene compounds were variable and inconsistent, and in some cases concentrations from the Tedlar-covered plot were elevated compared to ambient data. It was unclear if these observations resulted from contaminants in the snowpack sampling system, or from artifact

formation during storage; OVOC have been shown in previous studies to be sensitive to line losses and artificial enhancements. Consequently, compounds showing this behavior are not reported in this work.

There is some uncertainty in the recovery of the whole air samples for the Niwot Ridge study because no standard recovery experiments were conducted with this sampling manifold. All materials in contact with sample air have been found inert for ozone, CO_2, nitrogen oxide, water vapor, and N_2O. Furthermore, similar sampling methods used at Summit, Greenland, and South Pole, Antarctica, have been shown to transmit these trace gases without evident losses (Swanson et al. 2005). Therefore, it is unlikely that this sampling system would cause analyte losses of the volatile gases reported here.

Snowpack temperatures were measured at each sampling height with thermocouple wires, as described in Seok et al. (2009). Basic meteorology information used for data interpretations was recorded on a tower located at the Soddie; additional met data used were from the Ameriflux tower at the NWT C-1 site.

Results

Ambient air temperatures on the two sampling days were similar, with daytime maxima reaching −8°C on March 15, vs. −4°C on March 17. Total incoming, visible solar radiation was also similar, with daytime maxima reaching levels of ∼1,650 W m^{-2} on both days. A noticeable difference was seen in wind speeds, with winds recorded at <1 m s^{-1} during 10:00–18:00 h on March 15, whereas winds were sustained at ∼3–4 m s^{-1}, and 2–4 m s^{-1} on March 16 and 17, respectively.

Samples were collected during midday, between 11:00–16:00 h. Consequently, data are not expected to demonstrate significant diurnal influence caused by thermal or solar irradiance daily cycles. Therefore, results from samples collected at the same depth but at different times were merged. The range of concentration data for each of the compounds analyzed, broken up in subgroups for the ambient air samples, samples from the Tedlar-covered area, and from the natural snow tower, are summarized in Table 1. Analyzed gases showed differing behavior, with some exhibiting distinct concentration gradients. To better illustrate this behavior, measurements obtained from the same inlet heights were lumped together for both the natural and the Tedlar-covered site. Figure 2 displays measurements for a selection of gases that showed distinct differences in concentrations between the ambient air inlet and the snowpack samples. These data were organized by classes of compounds, with panel (a) displaying volatile inorganic gases and organic species, and panel (b) depicting halogenated compounds.

Discussion

Snowpack gas concentrations

Many of the analyzed gases (Fig. 2) show distinct concentration changes with measurement height, as well as differences between the natural and the Tedlar-covered plots. These obvious concentration enhancements/reductions are an indication for the snowpack and/or the soil serving as a source or sink of these gases. These gradients are also a consequence of the slower gas exchange inside the snowpack (compared to above the snow surface). Gas diffusivity values calculated within the snowpack are on the order of 10^{-5}–10^{-6} m^{-2} s^{-1} (Seok et al. 2009), which is 3–6 orders of magnitude lower than typical values seen above the snow. The slower gas transport within the snowpack allows for the formation of gas gradients that are large enough to be well discernable with the achievable precision of the applied measurement protocols. In essence, the snowpack behaves similar to a chamber experiment, allowing for highly sensitive studies of the chemistry and exchanges of gas species, without imposing artificial conditions that are inherent to most other enclosure experiments.

Closer inspection of data from samples collected on the two separate sampling days, March 15 and 17, showed that for a number of analyzed gas species significant differences were found in ambient levels and in their snowpack gradients. Fig. 3 displays this behavior for ethyne and CFC-12. Ethyne ambient levels dropped from a mean of ∼490 pptv on March 15 to ∼350 pptv on March 17, and this decline in ambient concentrations was paralleled by a drop in snowpack concentrations and gradients. A similar pattern was observed for CFC-12, albeit the change in

Table 1 Number of samples (in parenthesis), analyzed compounds, and range of their mixing ratios found in air sampled above the surface, and in snowpack air drawn at three depths over the Tedlar-covered soil, and at four depths over natural soil

Compound (units)	Ambient air (10)	Snow tower over Tedlar cover (22)	Natural snow tower (34)
Inorganic gases			
CO (ppbv)	141–167	147–192	11–94
CO_2 (ppmv)	401–490	567–777	989–2,791
COS (pptv)	442–474	344–426	48–251
CS_2 (pptv)	7.0–129	7–26	11–275
Hydrocarbons			
CH_4 (ppmv)	1.83–1.88	1.74–1.81	1.29–1.67
Ethyne (pptv)	345–533	322–493	174–347
Ethane (pptv)	1,816–2,718	1,819–2,571	1,553–2,268
Propane (pptv)	473–934	695–1,700	618–1,281
i-Butane (pptv)	66–153	189–374	80–245
n-Butane (pptv)	110–247	118–391	83–199
i-Pentane (pptv)	41–70	31–127	37–79
n-Pentane (pptv)	25–56	43–147	35–68
n-Hexane (pptv)	7–24	5–40	9–31
Isoprene (pptv)	38–164	12–28	14–166
Benzene (pptv)	82–160	62–156	9–60
Toluene (pptv)	28–105	38–100	5–113
Halogenated compounds			
CFC-12 (pptv)	531–552	514–551	480–525
CFC-11 (pptv)	252–262	248–260	231–252
CFC-113 (pptv)	79–83	70–85	67–78
H-2402 (pptv)	0.3–0.3	0.2–0.5	0.2–0.4
HFC 134a (pptv)	33–36	31–39	30–34
HCFC-22 (pptv)	166–175	155–169	131–158
HCFC-142b (pptv)	15–16	14–15	13–15
HCFC-141b (pptv)	18–20	15–18	13–18
$CHCl_3$ (pptv)	25–59	48–123	168–853
$MeCCl_3$ (pptv)	19–21	19–21	16–19
CCl_4 (pptv)	88–93	80–91	62–83
C_2Cl_4 (pptv)	5.8–8.2	6.3–13	4.3–8.2
CH_3Cl (pptv)	510–598	466–526	30–277
CH_3Br (pptv)	8.1–11	8.7–13	0.4–6.5
CH_3I (pptv)	0.2–7.3	24–68	0.4–10
CH_3CH_2I (pptv)	0.1–0.8	3.8–7.2	<0.1–2.0
CH_2Br_2 (pptv)	0.7–1.0	0.6–1.1	0.1–0.5
$CHBrCl_2$ (pptv)	0.2–0.3	0.2–0.2	0.2–0.5
$CHBr_3$ (pptv)	0.7–1.5	0.1–1.9	0.1–0.7
Ethyl chloride (pptv)	2.0–3.4	5.1–13	5.7–25
1,2-DCE (pptv)	7.2–11	4.4–19	0.2–6.6
Alkyl nitrates			
Me-ONO_2 (pptv)	2.3–3.5	0.4–9.1	0.1–2.9
Et-ONO_2 (pptv)	2.7–6.6	4.3–13	1–6.4
i-Pr-ONO_2 (pptv)	1.7–4.3	5.2–18	1.6–9.1

Table 1 continued

Compound (units)	Ambient air	Snow tower over Tedlar cover	Natural snow tower
n-Pr-ONO_2 (pptv)	0.6–1.0	0.7–3.2	<0.1–1.3
2-Bu-ONO_2 (pptv)	7.4–17	4.1–18	0.6–8.3
3-Pen-ONO_2 (pptv)	1.6–3.2	0.2–4.1	0.2–1.3
2-Pen-ONO_2 (pptv)	1.7–4.1	0.9–5.5	0.7–1.9
Others			
DMS (pptv)	4–7	3–15	7–49

ambient levels was significantly smaller, consistent with the much lower spatial and temporal variability of the long-lived chlorofluorocarbons in ambient air (Karbiwnyk et al. 2003). Similar patterns were observed for most other compounds with primary anthropogenic sources. While temperatures and radiation levels were similar on these 2 days, winds were significantly, i.e., 2–4 times higher, on March 16 and 17. From these comparisons, it appears that the higher winds brought in cleaner air, with lower levels of anthropogenic trace gases, and that similar to the ambient concentrations, snowpack levels were lower under these conditions. This effect is most likely attributable to the increased snowpack ventilation from wind pumping. Using primarily CO_2 data, Seok et al. (2009) present a thorough investigation of the dependency of snowpack gas concentrations at different snowpack depths on wind conditions. Their findings show the high sensitivity of trace gas concentrations in interstitial air on the wind conditions above the surface, with large decreases of snowpack [CO_2] during high wind conditions. The gas observations from the canister sampling presented here further support these conclusions, as the general behavior of concentration changes are in full agreement with the Seok et al. (2009) findings.

The relative effect of wind pumping on ambient and snowpack gas gradients varied among the analyzed gases depending on absolute ambient levels and their variability, and on their source/sink strength in the snowpack. Subsequent discussions in this paper are based on the combined, entire data set; this procedure preserved inclusion of data from a higher number of samples (i.e., complete data set) and avoided a somewhat arbitrary division of compounds for these further analyses.

Three different principle behaviors can be seen among gases listed in the combined data in Table 1. Several gases exhibit higher than ambient concentrations in the snowpack. A second group shows lower levels in the snow, and a third group of compounds appears to be unchanged from atmosphere to snowpack. The included measurements from the Tedlar-covered area illustrate that generally gas concentrations over the Tedlar-covered area were in closer agreement to ambient air levels than measurements from the natural snowpack. Slight deviations from ambient concentrations in the Tedlar-covered data likely arise from the fact that the Tedlar cover and the excavation around the plot a few days prior to the sampling suppressed most, but not 100% of the soil influences and advection from the bordering snowpack area.

Enhanced snowpack levels are most obvious for CO_2, where concentrations in the snowpack are 2–6 times higher than in air above the snow. The canister samples showed a CO_2 increase from 439 $\pm$ 33 ppmv in the atmosphere to 2,300 $\pm$ 440 ppmv at the base of the snowpack (Fig. 2a). This enhancement of CO_2 seen in the flask data is in agreement with the much more extensive CO_2 record from the four winters of in-situ measurements. Liptzin et al. (2009) present an in depth discussion of the NWT snowpack CO_2 records for 2006-2007, and show that, depending on snowpack thickness, CO_2 inside the NWT snowpack ranges from 2000 to 10 000 ppmv.

Along with CO_2 there are several other trace gases that show concentration increases in the snowpack (compared to the atmosphere). These species include two halogenated gases, i.e., chloroform ($CHCl_3$) and bromodichloromethane ($CHBrCl_2$), and dimethyl sulfide (DMS) (Fig. 2a, b).

There are a number of gases displaying lower concentrations in the snowpack than above the surface, indicative of the snow or the soil acting as a sink of these species. These gases commonly

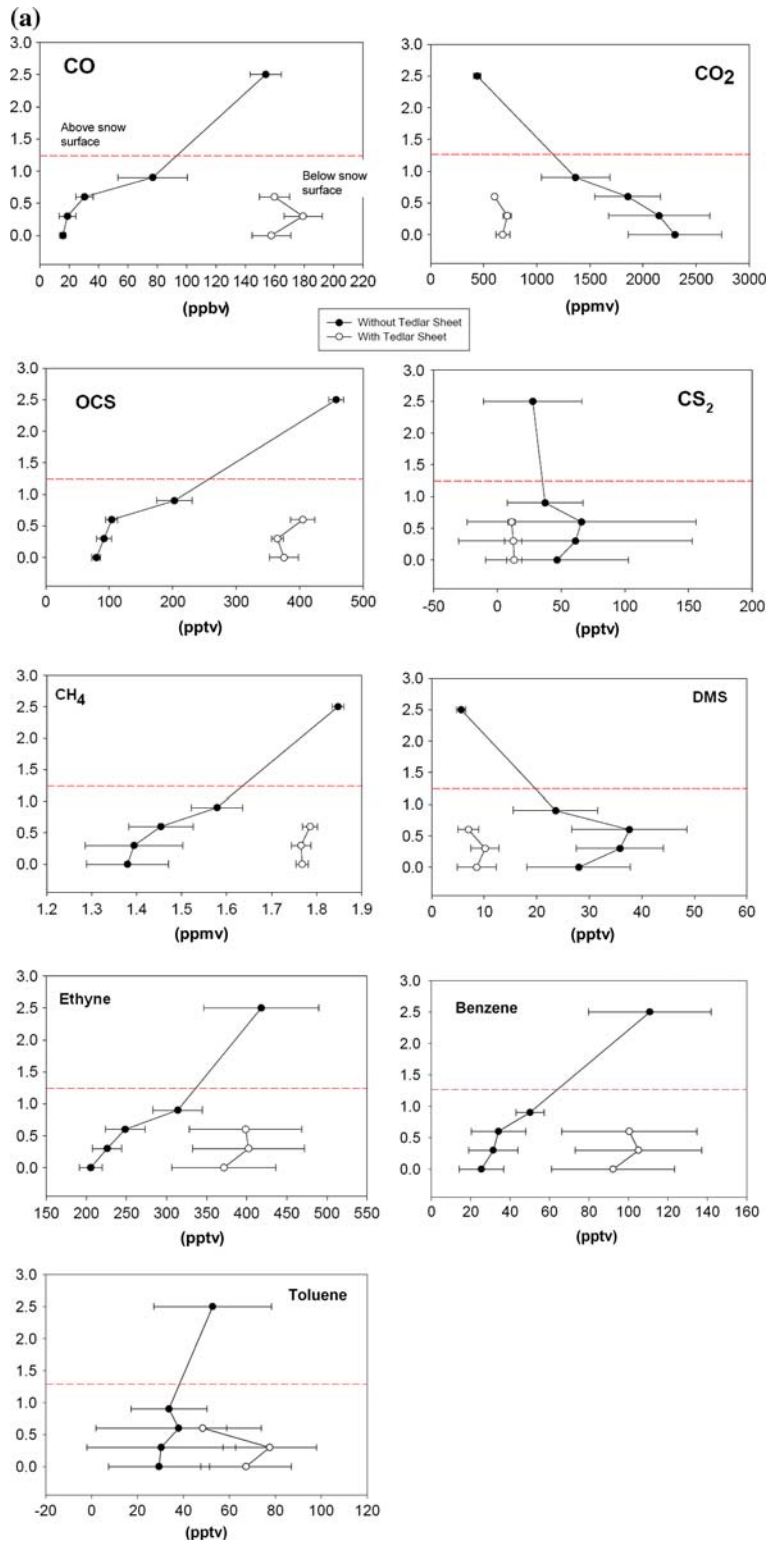

Fig. 2a Concentration profiles of CO, CO_2, COS, and CS_2, and for the organic compounds methane, dimethylsulfide, ethyne (acetylene), benzene and toluene at the snow-soil interface (0 cm), three levels above the ground inside the snowpack (30, 60, 90 cm) and above the snowpack (245 cm), with the y-axis scale indicating the distance from the soil surface (in meters). The snowpack height during the time of sampling was ~130 cm, shown by the *staggered line*. *Filled circles* depict samples collected from the natural snow tower, and *open circles* are data collected from the adjacent tower that was placed on the Tedlar sheet. Data are mean values from ~3–5 samples collected from each inlet, with error bars indicating the standard deviation of each subset of data

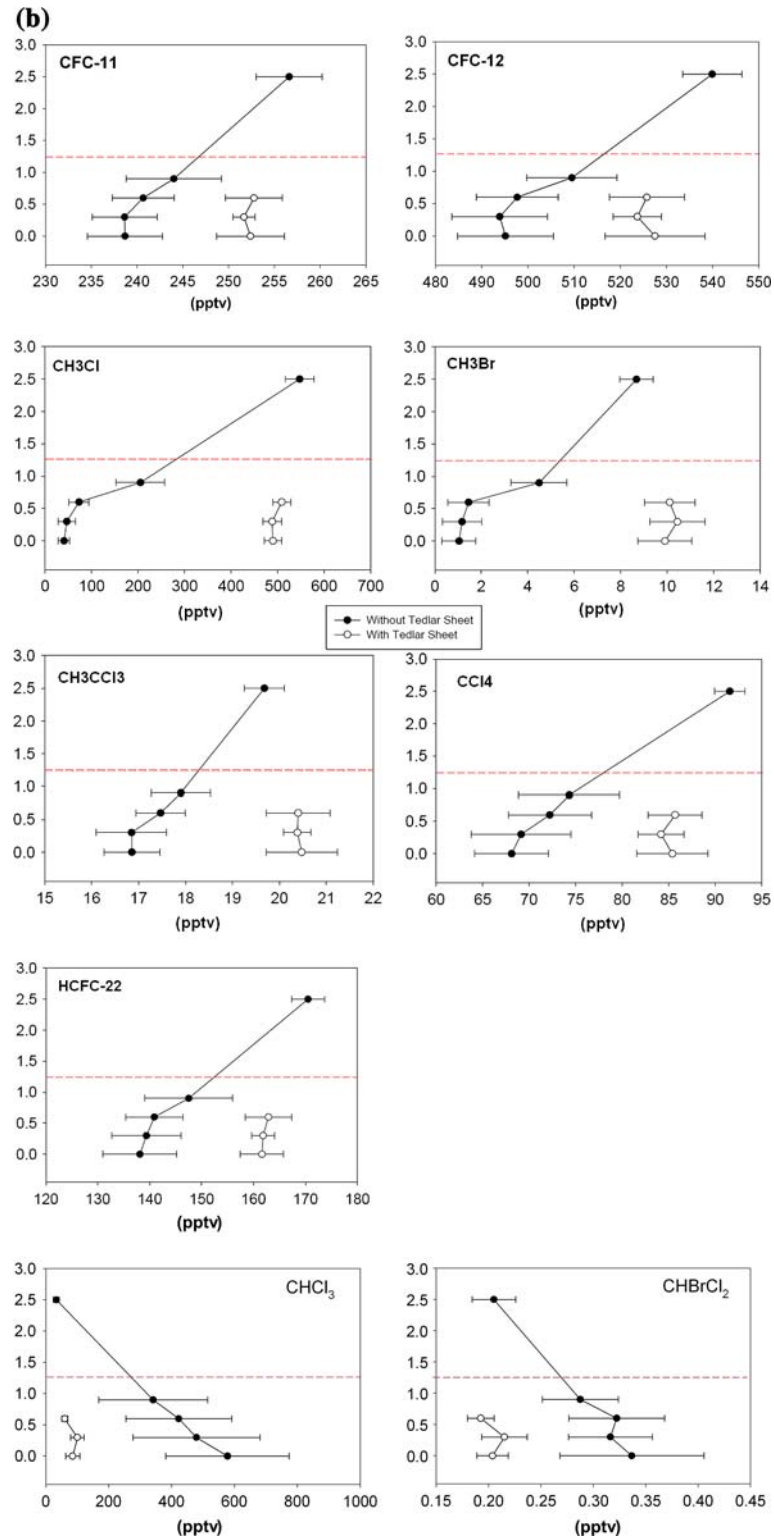

Fig. 2b Same as Fig. 2a for the halogenated compounds CFC-11, CFC-12, CH_3Cl, CH_3Br, CH_3CCl_3, CCl_4, and HCFC-22, showing uptake to the snowpack, as well as for $CHCl_3$ and $CHBrCl_2$, which show an efflux out of the snow

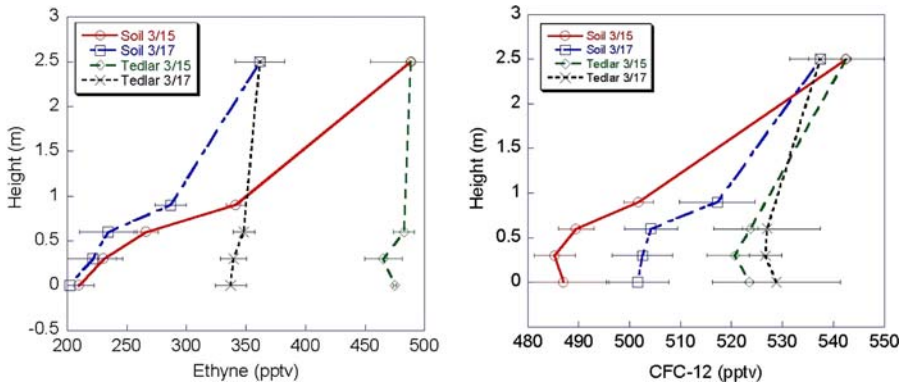

Fig. 3 Comparison of ethyne and CFC-12 snowpack gradient data (mean and standard deviation of measurements from each inlet) obtained from both snow towers on March 15 and 17

display a near monotonic increase in concentration with sampling height above the soil, as shown in Fig. 2. This list of compounds includes inorganic gases such as CO and COS; hydrocarbons, e.g., methane, ethyne, ethane, benzene; and a suite of halogenated compounds, e.g., CFC-11, CFC-12, CH_3Cl, CH_3Br, CH_3CCl_3, and CCl_4. Please note that for all of these compounds their lower snowpack levels represent statistically significant decreases. For instance, the CFC-11 gradients into the snowpack shown in Fig. 2b averaged ~6–9% of the mean above the snow, which is well above the 0.5% relative precision of the CFC-11 measurement (Colman et al. 2001).

Snowpack fluxes

Applying Fick's gas diffusion law, fluxes were quantified using the gas gradient data and assumptions on the gas diffusivity, which relies on snowpack density, temperature, and the particular gas diffusion coefficient. Gas fluxes were calculated using the mean concentration gradient between inlet height combinations in the data shown in Fig. 2. For the 245–90 cm gradient the ambient air measurement at 245 cm was assumed to represent the concentration value at the snow surface; fluxes were also calculated from the 90–60 cm, 60–30 cm, and 30–0 cm gradients. We only report flux results for cases where two conditions were met: (1) A concentration increase or decrease between the ambient and the snowpack measurements was clearly identifiable in the graphical analyses shown in Fig. 2. (2) Data from the measurements over the Tedlar cover were in closer agreement with the ambient data than the measurements from the natural snow tower. Snowpack temperature was set at 273 K, which reflects the isothermal March snowpack conditions at this site (Seok et al. 2009). The snow density was set to 353 kg m^{-3}, which was the mean value determined in 21 layers in a snow pit near the flux tower on March 31. Available diffusion coefficients from literature, as listed in Table 2, were applied. As Seok et al. (2009) showed that mean/median values from multiple gradient calculations yield a more representative flux value than measurements from a single gradient interval, mean, median, and standard deviation of the four individual gradient flux determinations were determined; these results are expected to represent the best estimate of actual snowpack fluxes. Results from these flux determinations are shown in Table 2. According to common convention, upwards fluxes (emissions) are given as positive values, and surface uptake fluxes (deposition) as negative. Gases are grouped into an emission flux and an uptake flux category. Within each category, gases are listed by the magnitude of the median flux result, in order of declining molar flux, with a subdivision according to a 10^3 flux unit division.

Snowpack is a porous medium that allows gases to flow in the vertical and horizontal by diffusion processes as well as by forced ventilation (mostly advection caused by wind pumping). In the companion paper to this publication Seok et al. (2009) demonstrate that for the NWT experiment the sampling procedure itself constituted only a minor influence on the gas gradients in this snowpack. The diffusive gas flux inside the snow is determined by the gas concentration gradients. Using all-winter season and multiple year data, Seok et al. (2009)

Table 2 Snow-atmosphere gas fluxes calculated from concentration gradients with comparison to previous literature

		Snowpack flux								
		Gradient interval						Literature comparison		
	Diffusion coefficient (m^{-2} s^{-1})[a]	Surface-90 cm	90–60 cm	60–30 cm	30–0 cm	Median ± standard deviation	Units (mol m^{-2} s^{-1})	Flux	Reference	Seasonally snow-covered soil lifetime estimate (years)
Emission flux										
CO_2	1.4E-05[b]	745	529	316	160	422 ± 255	10^{-9}	20–800	Suzuki et al. 2006	
$CHCl_3$	7.6E-06[c]	136	48	33	58	53 ± 46	10^{-15}	155	Swanson et al. 2005	
DMS	9.2E-06[d]	9.8	10	−1.3	−5.6	4 ± 7.9	10^{-15}			
CS_2	8.9E-06[b]	5.5	20	−3.3	−10	1 ± 12.9	10^{-15}	−65	Swanson et al. 2005	
$CHBrCl_2$	6.8E-06[e]	33	22	−4	13	17 ± 15	10^{-18}			
Uptake flux										
CH_4	2.0E-05[b]	−306	−190	−90	−22	−140 ± 124	10^{-12}	−(86−34)	Sommerfeld et al. 1993	3,400
CO	1.8E-05[b]	−80	−65	−16	−4	−41 ± 37	10^{-12}	Bi-directional	Constant et al. 2008	
CH_3Cl	1.1E-05[d]	−217	−111	−22	−5	−67 ± 97	10^{-15}	154	Swanson et al. 2005	2,100
Ethane	1.2E-05[d]	−122	−178	−4	−29	−75 ± 81	10^{-15}	50	Swanson et al. 2005	7,800
COS	1.1E-05[d]	−161	−83	−10	−10	−46 ± 72	10^{-15}	−65	Swanson et al. 2005	2,500
Ethyne	1.4E-05[d]	−80	−72	−25	−22	−48 ± 30	10^{-15}			2,300
CFC-12	7.9E-06[f]	−14	−14	−4.4	1.4	−9 ± 8	10^{-15}			15,000
Benzene	9.3E-06[c]	−26	−9	−2	−4	−6 ± 11	10^{-15}	−0.9	Swanson et al. 2005	4,900
HCFC-22	1.0E-05[g]	−13.4	−7.7	−1.8	−1.5	−5 ± 5.7	10^{-15}			9,300
CFC-11	7.7E-06[c]	−5.7	−2.0	−1.2	0.0	−2 ± 2.5	10^{-15}	0.2	Swanson et al. 2005	41,000
CH_3Br	1.4E-05[c]	−3.4	−3.3	−0.3	−0.1	−2 ± 1.8	10^{-15}	−0.3	Swanson et al. 2005	1,300
CCl_4	6.4E-06[c]	−6.5	−1.1	−1.5	−0.5	−1 ± 2.8	10^{-15}	−0.9	Swanson et al. 2005	18,100
1,2-dichloroethane	7.7E-06[h]	−1,854	−210	−566	−432	−499 ± 740	10^{-18}	−103	Swanson et al. 2005	42,000
CFC-113	6.6E-06[c]	−2,791	280	−784	−71	−427 ± 1,373	10^{-18}	−198	Swanson et al. 2005	49,000
$MeCCl_3$	7.0E-06[c]	−732	−238	−338	3	−288 ± 306	10^{-18}	−122	Swanson et al. 2005	18,000
HCFC-141b	7.7E-06[c]	−1,062	117	−275	−59	−167 ± 520	10^{-18}	−78	Swanson et al. 2005	29,000
HCFC-142b	8.7E-06[c]	−565	−217	−96	13	−157 ± 251	10^{-18}	−54	Swanson et al. 2005	25,000
CH_2Br_2	8.0E-06[c]	−265	−68	−29	−25	−49 ± 114	10^{-18}	−73	Swanson et al. 2005	4,500
$CHBr_3$	6.8E-06[c]	−279	−30	−19	−15	−25 ± 129	10^{-18}	−13	Swanson et al. 2005	11,000

Diffusion coefficient references: [a] Diffusion coefficients are reported at 273 K, 101.3 hPa. Reported literature data were converted to these conditions according to Musselman et al. (2005), [b] Massman (1998), [c] Nelson (1971), [d] Swanson et al. (2005), [e] Cowie and Watts (1971), [f] Calculated using Chatman and Enskog equation (Bird et al. 2002), [g] Generic, estimated value, [h] Lugg (1968)

present an in-depth evaluation of this method for the NWT conditions. They conclude that the quality of flux results improves when gradient data from multiple inlet combinations are considered, and when measurements are repeated throughout the season. This is probably due to the fact that inhomogenous vertical conditions in porosity and turtuosity, which can be caused by ice and crust layers, can influence the vertical gas transfer, and that such effects are not considered in the Fick's Law calculation. Fluxes calculated from continuous, in-situ measurements of CO_2 (Liptzin et al. 2009), nitrogen oxides (Helmig et al. 2009), and N_2O (Filippa et al. 2009) showed a surprisingly high day-to-day variability. Further analyses presented in these papers show that these fluctuations were predominantly caused by snowpack ventilation from pressure pumping (caused by winds), which reduces the gas gradients and flux results from the diffusion calculation (which does not consider the wind pumping effect on gradients). Further analysis of this dependency showed that for a mid-winter period at NWT, fluxes may be underestimated on average by 36%. When data were integrated over longer time periods (averaging over the variable wind conditions), gas fluxes during the mid-winter period were relatively constant, with only a slow, gradual increase in fluxes observed during the early to mid winter period. During snowmelt in late April/May, more significant increases and fluctuations were related to the increase in the soil volumetric water content, which caused a burst in microbial activity during that period. Assuming that similar processes drive the exchanges of the gases reported in this paper, it appears reasonable to expect that their fluxes during the March intensive period are representative for most of the snow-covered season until the onset of snow melt. Winds, measured on a nearby tower at 6 m above ground, were on average 2.6 ± 2.7 m s^{-1} during the canister sampling period, although, as mentioned above, conditions were quite different on the two sampling days. On average, however, these winds are similar to the conditions during the case study presented by (Seok et al. 2009). Consequently, it is reasonable to assume that flux results reported here, lacking a correction for the wind pumping dependence, should be considered lower estimates, with actual flux values likely being on the order of 30-40% higher.

Interpretation of concentration and flux results

Emission fluxes

The largest of all gas fluxes was found for CO_2, with an emission rate of 0.42 μmol m^{-2} s^{-1}. This calculation compares reasonably well with the in-situ data, which resulted in mean wintertime CO_2 fluxes of 0.71 and 0.86 μmol m^{-2} s^{-1} for 2006 and 2007, respectively (Liptzin et al. 2009). This finding is also in qualitative agreement with numerous previous studies that reported similar magnitude wintertime CO_2 efflux from high-elevation sites (Sommerfeld et al. 1993; Brooks et al. 1997).

In addition to CO_2, four other volatile gases, i.e., DMS, CS_2, chloroform, and $CHBrCl_2$, were found to exhibit a positive flux from the NWT snowpack, with exchange rates for these species ranging from 0.02×10^{-15} to 50×10^{-15} mol m^{-2} s^{-1} (Table 2). The concentration profiles for these species (Fig. 2) show that in general all of these gases exhibit their highest concentrations at the lowest snowpack inlet, which implies that the subnivial soil is the determining source. Vegetated soils and leaf litter have been reported as a contributing emission source in other studies for chloroform (Hoekstra et al. 2001; Laturnus et al. 2002), dimethylsulfide (Kesselmeier and Hubert 2002; Yi et al. 2008), and carbon disulfide (Steinbacher et al. 2004). The review of this literature indicates that the efflux of these species is particularly prominent under anaerobic and moist conditions.

The only other study reporting fluxes of any of these gases from a snowpack was the experiment at the NWT Mountain Research Station in the winter of 2003 (hereafter referred to as NWT-2003). Reported chloroform fluxes from these two studies are within a factor of three. For CS_2, a deposition flux was seen in the NWT-2003 experiment, whereas here we found a release from the snowpack. Other previous research has pointed out the bi-directional flux behavior of carbon disulfide, as both soil uptake and release were seen (Steinbacher et al. 2004) at the same site. For $CHBrCl_2$ previous literature has reported that algae produce this gas, causing oceanic emissions (Schall et al. 1994; Warwick et al. 2006a). To the best of our knowledge, our $CHBrCl_2$ flux observations are the first reports for emissions of this compound from a snow-covered site.

For the polar snow at Summit, a series of gases, including CH_3Br, CH_3I, C_2H_5I, ethene and propene, were found to be photochemically produced in sunlit snow (Swanson et al. 2002). These gases showed their highest concentrations just below the snow surface, supporting the hypothesis that their formation was driven by solar irradiance and was predominantly occurring in the first few centimeters below the snow surface. Similar to the Summit observations, several gases exhibited their highest levels in air collected from the upper inlets on the NWT snow tower, namely DMS, CS_2, and ethyl chloride. However, these gases did not show significant enhancements in air collected over the Tedlar sheet; this would be expected if their production was driven by photochemical processes in the snow rather than from soil emissions. We did, however, observe enhanced levels for a number of gases, including alkenes, iodated compounds, and alkyl nitrates, in air collected from the Tedlar-covered plot. However, with currently available information it is uncertain if these enhanced levels were caused by photochemical formation in the snow or from an artifact in the experiment.

Uptake fluxes

Following the aforementioned criteria, 19 gases were found to be taken up by the snow, with calculated uptake rates spanning six orders of magnitude. The overall largest uptake flux was observed for methane, followed by carbon monoxide and methyl chloride. Three other non-methane hydrocarbons, i.e., ethane, ethyne, and benzene, were found to be taken up by the snowpack/soil. Thirteen halogenated gases, including both fully and partially chlorinated and brominated species, i.e., CFC and hydrochlorofluorocarbons (HCFC), were found with negative fluxes.

Linear flux behavior with height suggests that soil processes are the predominant sink for the uptake of these gases (e.g., acetylene, benzene, CCl_4); these cases will be discussed in more detail below. There are also a number of cases where gradients appear to be non-linear, with relatively larger reductions seen near the surface. This gradient profile translates into a flux divergence, with fluxes becoming smaller deeper in the snow. This feature is most apparent for methane and several of the halogenated gases, including methylchloride, and methylbromide (Fig. 3; Table 2). This behavior could imply that a chemical sink in the upper snow layers may contribute to the loss of these compounds. A series of recent investigations (Anastasio et al. 2007; Beyersdorf et al. 2007; France et al. 2007) have pointed out the significant oxidation potential of sunlit snow. These studies demonstrated heterogeneous production of the hydroxyl radical from snow impurities, with hydrogen peroxide and nitrate being important substrates for this radical formation. Other ongoing research has also pointed out the role of halogen chemistry in polar snow. In summary, this research has consistently shown that sunlit snow supports very active photochemistry. Most research on snowpack oxidation chemistry has been conducted at polar sites, and it is uncertain how these findings relate to the interpretation of our observations and how the polar snow chemistry could potentially explain the apparent gas losses seen in the mid-latitude NWT snowpack.

Soil uptake has been reported and enumerated for a number of these gases, see for instance published reports and references therein for methane (Curry 2007), CO (King and Crosby 2002), COS (Kesselmeier et al. 1999), methyl bromide (Varner et al. 1999; Serca et al. 1998), methyl chloride (Keppler et al. 2005), and methyl chloroform (Wang et al. 2006b). Albeit, exchanges of a number of these chemical fluxes can be bi-directional, depending on landscape type, soil and environmental conditions. This bi-directional behavior has been observed, e.g., for CO (Khalil and Rasmussen 2000; King and Crosby 2002), CH_4 (Wuebbles and Hayhoe 2002), and some halogenated compounds such as CH_3Br (Cox et al. 2004; Warwick et al. 2006b), CCl_4 (Happell and Roche 2003), and CH_3Cl (Wang et al. 2006a; Rhew and Abel 2007).

There are very few studies from snow-covered environments that allow for a comparison with our flux data; available reports have been included in Table 2. In agreement with our data Sommerfeld et al. (1993) observed methane uptake through a Wyoming snowpack. Our fluxes are $\sim$2–5 times higher than their determined mean flux values for three snow-covered sites [i.e., $-(30-86)$ mol s^{-2} s^{-1}]. Similar to the methane sink, the NWT observations show that other non-methane hydrocarbons are taken up by the snowpack. Losses were clearly discernable for ethane, acetylene, and benzene. To the best of our knowledge,

neither of these compounds has previously been reported as having a snow or winter soil sink.

Most of our observed flux directions are consistent with the findings reported by Swanson et al. (2005). Their data resulted from samples collected during a one-day study at the ~450 m lower elevation NWT Mountain Research Station, and from a freshly excavated snow pit. Similar to our data, their results pointed towards a rigorous gas exchange through the NWT snowpack. Comparison of these two data sets shows that for the majority of compounds (13) similar flux behavior was observed. In most cases our newer data from the Soddie site show higher snow uptake rates than the Swanson et al. (2005) measurements. For four compounds (CS_2, methyl chloride, ethane, CFC-11) these two studies disagree in the flux direction; for instance methyl chloride showed an opposite gradient and flux from what it showed in the NWT-2003 data set, when it was enhanced in the snowpack, reaching 1,275 pptv, 690 pptv higher than ambient levels. As mentioned above, other literature has pointed towards possible emission and/or uptake exchanges for CH_3Cl as well as for CS_2. The fact that both of these processes were observed at two sites that are in close proximity, albeit having different soil, vegetation, and snow cover characteristics, poses the question of what underlying processes control these exchanges.

Our new data, involving multiple day and multiple height measurements as well as comparison with a Tedlar-covered area, add not only new confidence, but also better constraints on the direction and magnitude of the fluxes of observed gas species. In particular, these findings confirm the previously reported emission flux of chloroform from this snow-covered environment, as well as the surface uptake of many anthropogenic halogenated gases. Many of these species are important contributors to the atmospheric halogen burden effecting stratospheric ozone depletion. Since these data point towards a contribution from snow-covered environments in the atmospheric removal of these gases, we developed a first order estimate of how significant this sink would be on a global scale. This estimate is based on the assumption that all seasonally snow-covered soils would exhibit the order of magnitude fluxes that were determined for NWT. First, the global mean area covered by seasonal snow (excluding permanently snow-covered land in Greenland and Antarctica) was calculated using the simulated snow cover from the chemistry-climate model ECHAM5/MESSy [which has been found to reasonably agree with ground-based and remote-sensing observations (Roesch and Roeckner 2006)]. The seasonally snow-covered area of 1.4×10^{13} m^2 represents about 10% of the global land mass. Next, the mean fractional snow-cover length was determined and applied to this surface area. We then calculated the atmospheric burden from measured mixing ratios, applied the determined flux results in Table 2, and calculated the lifetime (drop to 1/e) resulting from this deposition flux alone. As enumerated above, these values based on the diffusion model calculation (without applying a wind pumping correction) will result in a lower estimate of the gas flux. Results from this calculation are included in the last column in Table 2. These calculated lifetimes; all at >1,000 years are rather long compared to published atmospheric residence times of these compounds, which vary from a few years for HCFC and methyl halides to ~100 years for the most persistent CFC. These data represent the sink to seasonally snow-covered soil area, during the snow-covered days only. As these fluxes are determined predominantly by soil uptake, it is conceivable that fluxes of similar magnitude exist during the non-snow-covered period, as well as for soils in other places on Earth that never experience snow-covered conditions. Applying these fluxes to all land and year-round would place the uptake rates at ~20 times above the snow cover-only estimate. This would result in soil uptake lifetimes of ~1/20 compared to the values listed in Table 2, which brings a number of these lifetimes into a range that warrants consideration in the atmospheric budget of these gases.

Conclusions

The snowpack sampling technique and resulting concentration gradient measurements from this study proved to be a highly sensitive method for elucidating soil-snow-atmosphere gas exchange processes. Gas diffusivity within the snowpack is significantly slower than above the surface, which results in chemical snowpack concentration gradients that can be well resolved with available analytical techniques. Using Fick's Law diffusion method allows estimation

of fluxes from these gradients with sensitivities approaching $\sim 10^{-15}$ mol s^{-1} m^{-2}. These flux measurements represent some of the most sensitive determinations for these gas exchanges at the soil-snow-atmosphere interface that have been reported to date, and allowed the investigation of gas exchanges that hitherto have not been accomplished by other means. The demonstrated capability of this experiment is a strong motivation for further research in this area.

These experiments resulted in new insights into snowpack chemistry and soil-atmosphere gas exchange processes and expand upon work in previous literature, in particular by Swanson et al. (2005). Results further illustrate the active exchange of many gases between the atmosphere and snow-covered soil, and how winter fluxes contribute to the atmospheric budgets of these species. Besides the well documented emissions of CO_2, the NWT snowpack was also found to be a source for chloroform, DMS, CS_2 and $CHBrCl_2$.

A series of 19 other gases was found to be taken up by the snow. For many of these species (CO, CH_3Cl, ethane, ethyne, benzene, and thirteen halogenated compounds) this and the Swanson et al. (2005) work are the only published reports that demonstrate this surface sink. In particular, these new data further exemplify the snow surface sink strength for a series of long-lived halogenated compounds, including CFC-11 and CFC-12, HCFC, and brominated gases that play an important role in stratospheric ozone depletion. As these compounds are regulated under the Montreal Protocol, a full understanding and quantitative description of their soil and snow exchanges are important. To date, soil sink processes have been incorporated in assessments of atmospheric budgets for CH_3CCl_3 and CCl_4, but not for other ozone-depleting compounds, e.g., CFC-11 and CFC-12, that we found to be taken up by the NWT snowpack.

The apparent flux divergencies in the NWT snowpack gradient data for methane, and several of the halogenated gases, including methylchloride, and methylbromide, suggest that photochemical destruction in the uppermost layers of the snowpack may be contributing to the surface uptake of these compounds.

The companion papers in this special issue take a closer look at the biogeochemical dependencies of the CO_2, NO + NO_2, and N_2O production and efflux. These discussions conclude that the NWT site is characterized by remarkably high wintertime, subniveal microbial activity. Wintertime gas exchanges constitute significant fractions of the annual gas budgets for these species. The fact that wintertime soil microbial processes appear to be enhanced at NWT is likely due the constant, warm (i.e., near-freezing) wintertime temperature conditions for the 6+ months of snow cover, and the relatively constant moisture conditions (contrasted by highly variable and overall dry summertime conditions), which promote high microbial activity. The research reported in this paper underscores that these subnivial soil processes are causing the exchange of many other inorganic and organic trace gases. It seems likely that this includes further gas species of interest that were not captured by our particular experimental protocols.

Snow cover exhibits a wide range of conditions. Chemical snow composition, physical properties, the length of the snow-cover season, depth of snowpack, and substrate below the snow can all play important roles in determining chemical processing and surface exchanges. Comparison with available data from other sites suggests that gas exchange rates through the snowpack at NWT are relatively high compared to reports from other environments. Given the lack of comparison studies it is uncertain how representative the NWT data from this 3-day study are for year-round conditions and for other snow-covered landscapes. Further experiments at other sites, with preferably all-winter long observations are needed to clarify the representativeness of these data. Particular attention should be paid to high elevation ecosystems, as here wintertime soil processes are likely to constitute a more significant fraction of the annual soil activity. Quantitative descriptions of these gas exchanges will also be important for predictions of how changes in snow cover, both on land and on ice, will impact the exchange rates and budgets of these gases.

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